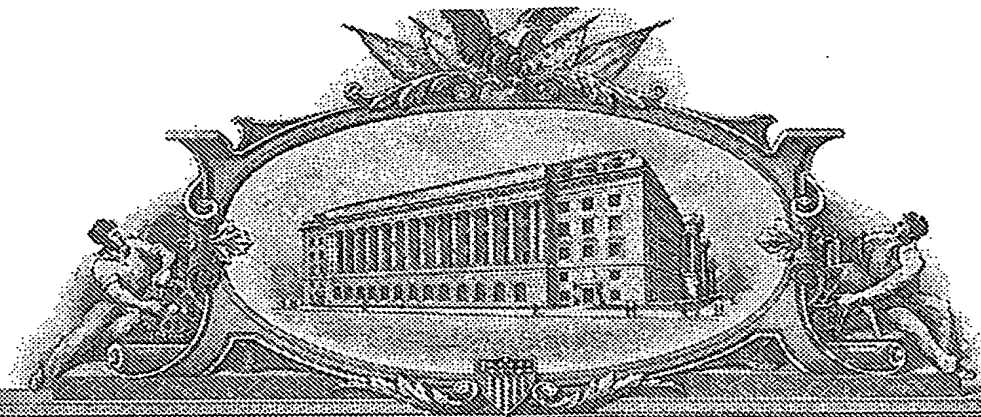


1339199



THE UNITED STATES OF AMERICA

TO ALL TO WHOM THESE PRESENTS SHALL COME:

UNITED STATES DEPARTMENT OF COMMERCE

United States Patent and Trademark Office

June 28, 2005

THIS IS TO CERTIFY THAT ANNEXED HERETO IS A TRUE COPY FROM THE RECORDS OF THE UNITED STATES PATENT AND TRADEMARK OFFICE OF THOSE PAPERS OF THE BELOW IDENTIFIED PATENT APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A FILING DATE.

APPLICATION NUMBER: 60/466,556

FILING DATE: April 28, 2003

RELATED PCT APPLICATION NUMBER: PCT/US04/12965



Certified by

Under Secretary of Commerce
for Intellectual Property
and Director of the United States
Patent and Trademark Office

1064 U.S. PTO
01/00/01

05-01-60465556-042803

\$ 15.15


Please type a plus sign (+) inside this box 

Approved for use through 10/31/2002. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

PROVISIONAL APPLICATION FOR PATENT COVER SHEET

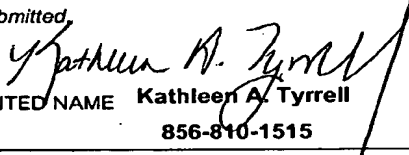
This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

U.S. PTO
60/466556

| INVENTOR(S) | | | | | |
|---|------------------------|--|--|-----|--|
| Given Name (first and middle (if any)) | Family Name or Surname | Residence (City and either State or Foreign Country) | | | |
| Yury Steven M. | Gogotsi Kurtz | Ivyland, PA Haddonfield, NJ | | | |
| <input type="checkbox"/> Additional inventors are being named on the _____ separately numbered sheets attached hereto | | | | | |
| TITLE OF THE INVENTION (280 characters max) BORON NITRIDE-ALUMINUM NITRIDE (BAN) INTERFACES AND COATINGS AND METHODS FOR THEIR PRODUCTION AND USE | | | | | |
| Direct all correspondence to: | | | | | |
| <input checked="" type="checkbox"/> Customer Number 26259 | |  | | | |
| OR Type Customer Number here | | 26259 | | | |
| <input type="checkbox"/> Firm or Individual Name | | PATENT TRADEMARK OFFICE | | | |
| Address | | | | | |
| Address | | | | | |
| City | | State | | ZIP | |
| Country | | Telephone | | Fax | |
| ENCLOSED APPLICATION PARTS (check all that apply) | | | | | |
| <input checked="" type="checkbox"/> Specification Number of Pages 20 | | <input type="checkbox"/> CD(s), Number | | | |
| <input checked="" type="checkbox"/> Drawing(s) Number of Sheets 3 | | <input checked="" type="checkbox"/> Other (specify) RETURN POSTCARD | | | |
| <input type="checkbox"/> Application Data Sheet. See 37 CFR 1.76 | | | | | |
| METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT (check one) | | | | | |
| <input checked="" type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. | | FILING FEE AMOUNT (\$) | | | |
| <input type="checkbox"/> A check or money order is enclosed to cover the filing fees | | \$80.00 | | | |
| <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge filing fees or credit any overpayment to Deposit Account Number | | 50-1619 | | | |
| <input type="checkbox"/> Payment by credit card. Form PTO-2038 is attached. | | | | | |
| The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government. | | | | | |
| <input checked="" type="checkbox"/> No. | | | | | |
| <input type="checkbox"/> Yes, the name of the U.S. Government agency and the Government contract number are: _____ | | | | | |

Respectfully submitted,

SIGNATURE


Kathleen A. Tyrrell
856-810-1515

TYPED or PRINTED NAME

TELEPHONE

Date

4/28/03

REGISTRATION NO.

(if appropriate)

Docket Number:

38,350

DRE-0075

USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT

This collection of information is required by 37 CFR 1.51. The information is used by the public to file (and by the PTO to process) a provisional application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 8 hours to complete, including gathering, preparing, and submitting the complete provisional application to the PTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, Washington, D.C. 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Box Provisional Application, Assistant Commissioner for Patents, Washington, D.C.

P19SMALL/REV05

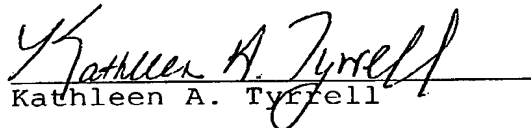
DRE-0075

CERTIFICATE OF EXPRESS MAILING

"Express Mail" Label No. EU804658483US
Date of Deposit: April 28, 2003

I hereby certify that this paper is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 C.F.A. 1.10 on the date indicated above and is addressed to the "BOX PROVISIONAL", U.S. Patent and Trademark Office, P.O. Box 2327, Arlington, VA 22202.

- 1) Patent Application Transmittal Letter (in duplicate);
- 2) Application consisting of 20 pages of specification, including 1 page of claims and 1 page of abstract;
- 3) Authorization to charge deposit account \$80.00 for filing fees;
- 4) Three sheets of informal drawings containing Figures 1-3;
- 5) Return Postcard.


Kathleen A. Tyrrell

DRE-0075

PATENT

Boron Nitride-Aluminum Nitride (BAN) Interfaces and Coatings and Methods for their Production and Use

Field of the Invention

5 Interface compositions comprising boron-aluminum-nitride and methods for coating ceramic fibers such as SiC with a boron-aluminum-nitride nanocomposite coating for use in ceramic matrix composites are provided. Such matrices are useful in high temperature applications and in oxidizing atmospheres such as in the aerospace industry and jet engine industry.

10

Background of the Invention

 The performance of ceramic matrix composites (CMC) depends greatly on the interaction between the composite components at mutual interfaces [Singh, R.N. J. Am. Ceram. Soc. 1989 72:1764-1767; Hull, D. An Introduction to Composite Materials, Cambridge Univ. Press, Cambridge, UK, 1981; Pirouz et al. Importance of Interfacial Strength on Fracture Toughness of Brittle Matrix Composites, Surfaces and Interfaces of Ceramic Materials, I.-C. Dufour et al. (eds.), 737-760, 1989]. Long and short fibers, whiskers, platelets and coarse equiaxial particles are used as reinforcement in composites, with long, continuous fibers improving mechanical properties most efficiently.

15 The most vulnerable component of SiC_f/SiC and other similar CMC systems, however, is the interface that separates the fiber and the matrix. If cracks exist in a composite in an oxidizing environment at an elevated temperature, the interface is exposed to the environment. To maintain the debonding and sliding properties that are required for good mechanical properties, either the interphase must be resistant to oxidation or the composite system must protect the interphase from oxidation. It is most desirable for the interphase to be an oxidation-resistant material; however, to date, no such interphase has proven effective at high temperatures for the SiC_f/SiC system. For non-oxide composite systems such as SiC/SiC composites, a single oxide interphase material has not been demonstrated, to date, to exhibit the weak interface behavior while being sufficiently compatible with the fiber and matrix materials at high temperatures.

20
25
30

 Although both the matrix and fiber components of older SiC/(Si/SiC) composites generally exhibit acceptably high resistance to oxidation, these composites become increasingly vulnerable to oxidation and consequent embrittlement whenever mechanical

DRE-0075

2

PATENT

or thermomechanical loads become large enough to crack the matrices. Even the narrowest cracks become pathways for the diffusion of oxygen. Typically, to impact toughness to an SiC/(Si/SiC) composite, the SiC fibers are coated with a material that yields at high stress to allow some slippage between the fibers and matrix. If oxygen infiltrates through the cracks to the fiber coating, then, at high temperature, the oxygen reacts with the coatings (and eventually with the fibers), causing removal of the interphase, undesired local bonding between fibers and the matrix and consequent loss of toughness. In addition, the resultant concentration of stress and deterioration of the fibers at the bonding locations give rise to failure of fibers. If the process of oxidation continues, then eventually the remaining fibers become unable to bear the load, causing the composite to fail at a stress appreciably below its initial (as-fabricated) ultimate strength.

Non-oxide ceramic systems of silicon carbide and silicon nitride are used as ceramic matrix materials of structural composites intended for high temperature service. These non-oxide ceramic systems combine excellent mechanical, chemical, thermal and physical properties. In particular, SiC matrices have utility in high temperature applications. For example, single phase refractory SiC ceramics are widely used at temperatures above 1500°C [Boecker, W.D.G., Ceram. Forum Int./ Ber. 1997 74:244-251, 1997.].

Oxide ceramic matrices used in industry typically comprise alumina and/or mullite. These non-oxide and oxide ceramic matrices are used in continuous ceramic fiber reinforced composites for gas turbine applications. Matrices used in this application need to have properties including high stiffness at low and high temperatures, high strength, high thermal and mechanical stability, high oxidation and corrosion resistance, small diameter for CMC fabricability and low cost for commercial viability.

The most commonly used non-oxide coatings for ceramic fibers are carbon and boron nitride [Rice, R.W. 1987 U.S. Patent 4,642,271; Singh, R.N. and Brun, M.K. Adv. Ceram. Mater. 1988 3:235-37; Cao et al. J. Am. Ceram. Soc. 1990 73(6):1691-99; Morscher et al. Ceram. Eng. Sci. Proc. 1997 18:7-8; Moore et al. J. Am. Ceram. Soc. 1997 80(5):1285-1288]. Carbon is the most widely used material for coatings because it is generally less expensive. The carbon coating must form a compliant layer that mitigates the effect of thermal stress: a thicker carbon coating reduces the thermal stresses better

than a thinner coating [Kerans, R.J. Control of Fiber-Matrix Interface Properties in Ceramic Matrix Composites, pp. 301-12 in Proceedings of High Temperature Ceramic Matrix Composites. Edited by R. Naslain, J. Lamon, and D. Doumeingts. Woodhead Publishing Limited, France, 1994]. However, carbon is easily accessible to oxygen at high
5 temperatures [Halblg et al. Oxygen Diffusion and Reaction Kinetics in Continuous Fiber Ceramic Matrix, Annual Cocoa Beach Conference and Exposition on Composites, *Advanced Ceramics, Materials and Structures*, Jan 20-24, 1998]. Accordingly, carbon-rich interfaces, produced either by natural fiber/matrix reaction (for NICALON or TYRANNO within silicate matrices) by solution method or by vapor deposition on fiber
10 precursors (such as in CVI SiC/SiC composites), present a low temperature ($\sim 400^\circ\text{C}$) limit in oxidizing environments (air, combustion products). In these CMCs, flash oxidation pretreatment of either the matrix itself or the fiber ends is used to prevent channeled carbon oxidation and provide protection from oxidation, but only in the absence of matrix microcracking [Pluckett et al. *J. Mater. Sci. Lett.* 1995 14:1223]. However, matrix
15 cracking always occurs under cyclic oxidation conditions and this method does not work for long-term high-temperature applications of composites.

Boron nitride has also been suggested as a potential fiber coating in SiC/SiC composites for high temperature application. A boron nitride coating allows the debonding of SiC fibers in reinforced SiC matrix composites. A process was recently
20 developed to produce a boron nitride rich region on the surface of Nextel 312 fibers [Campbell, S.S. and Gonszy, S.T. *Ceram. Eng. Sci. Proc.* 1994 327-336; Campbell, S.S. and Gonszy, S.T. *Ceram. Eng. Sci. Proc.* 1994 337-343]. The process is accomplished by heating the boria containing fibers to high temperatures in an atmosphere containing ammonia. The resulting BN-rich region is not an external, distinct coating, but rather a
25 thin (about 100A) region integral to the individual filaments [Sikonia, J. Nitrided Nextel 312 Fiber, IWG Workshop, 10-11 June 1997, WPAFB, OII 97].

However, BN is not stable in oxidizing environments and forms a liquid oxide B_2O_3 above 450°C . The presence of B_2O_3 leads to a series of synergistic reactions. For example, it can enhance SiO_2 formation from SiC. The SiO_2 and B_2O_3 can then react to
30 form stable borosilicates such as $\text{SiO}_2\text{-B}_2\text{O}_3$ which is eutectic at 372°C [Roth et al. *Phase Diagrams for Ceramists*, VI, Am. Ceram. Soc., Westerville, OH, 1969, p. 156]. This

situation occurs in a composite when the BN fiber coating has ready access to oxygen. These reactions lead to fiber consumption and degradation of fiber properties as well as fiber/matrix bonding, which then degrades the mechanical properties of the composites at elevated temperatures [Henager, C.H., Jones J. Cer. Eng. Sci. Proceedings 1992 13(7-8):411-19]. Thus, while BN has improved oxidation resistance over carbon coatings, there are many stability problems associated with its use, especially at intermediate temperatures and in the presence of water vapor [Petrak, D.R. CMC Interface Studies at Dow Corning, IWG Workshop, 10-11 June 1997, WPAFB, OH; Morscher et al. Ceram. Eng. Sci. Proc. 1997 18:7-8; More et al. The Stability of BN-containing CMCs Exposed to Oxygen and Water Vapor in the Temperature Range 425-1150°C, Abstract of the 193 Meeting of the Electro-Chemical Society, Abstract 812, 98-1, San Diego, 1998]. These stability issues of BN are related to several factors, including BN crystallographic structure, extent of crystallization, interface reactions, and impurity content, especially O [Ailey et al. Stability of BN Interfacial Coating During Oxidation and Exposure to Water Vapor, Annual Cocoa Beach Conference and Exposition on Composites, Advanced Ceramics, Materials and Structures, Jan 20-24, 1998; More et al. The Stability of Various BN Interfacial Coating in SiC/SiC Composites Exposed to Oxygen and Water Vapor in the Temperature Range 425-950°C, IWG Workshop, WPAFB, OH, 10-11 June 1997]. In particular, water vapor that is always present in significant amounts in combustion environments results in a very fast removal of the interfacial layer. The BN phase is very sensitive even to small amounts of water vapor in the oxidizing gas stream. This sensitivity is due to formation of highly stable $H_xB_yO_z$ (g) species from the reaction of water vapor and B_2O_3 . A low processing temperature BN fiber coating volatilizes readily in the presence of water vapor [Morscher et al. Ceram. Eng. Sci. Proc. 1997 18:7-8]. Less volatilization occurs with BN materials processed at high temperatures and/or doped with silicon. An examination of BN coated SiC fibers in a SiC matrix illustrates recession of BN in water vapor containing environments. This process is described with gas phase transport of $H_xB_yO_z$ (g) out of pores in the SiC matrix. In addition, there exist no inexpensive method to produce low-cost BN coatings on SiC fibers and no method that would produce these coatings without bridging the fibers in the tow or fabric.

Thus, the use of non-oxide CMCs in high temperature structural applications is presently limited by the environmental instability exhibited by conventional interphase materials such as C and BN fiber coatings.

Strategies currently used for oxide/oxide systems have attempted to replicate some of the microstructural features of the above-described nonoxides using phases with a low-cohesion layer-plane to form an oriented crystal interface by *in-situ* reaction between a simple fiber coating and surrounding matrix [Morgan, P.E.D. 1992 U.S. Patent 5,137,852; Cinibulk, M.K. Ceram. Eng. Sci. Proc. 1994 15(5):721-28; Lee et al. J. Am. Ceram. Soc. 1998 81(3):717-20]. An empirical search for complex oxides which have a high probability of low cohesion with matrix or fiber due to polarization of oxygen bonds by high valence cations, exemplified by vanadates, phosphates or niobates of type ABO_4 has also been performed. A large number of ABO_4 compounds such as tungstates, molybdates, tantalates and niobates are also being considered as fiber coatings for oxide-oxide systems [Goettler et al. Ceram. Eng. Sci. Proc. 1997 18(3):279-286]. Due to its easy cleaving basal planes, potassium calcium niobate ($KCa_2Nb_3O_{10}$) perovskite oxide is also being investigated as an interfacial coating material for oxide/oxide composites [Kim et al. Cleaving Oxides – KCN, IWG Workshop, 10-11 June 1997, WPAFB, OH].

Kerans [Control of Fiber-Matrix Interface Properties in Ceramic Matrix Composites, pp. 301-12 in Proceedings of High Temperature Ceramic Matrix Composites. Edited by R. Naslain, J. Lamon, and D. Doumeingts. Woodhead Publishing Limited, France, 1994] provides a review of some of the oxide interface concepts and interphase materials that have been considered for oxide composite systems. These include porous oxides, damaged oxides, easy-cleaving oxides, ductile interphases and segregant weakened interfaces. However, experimental results are relatively scarce in terms of validating the usefulness of these interface concepts.

Use of a monazite ($LaPO_4$) coating in oxide-oxide compositions was recently disclosed [Kuo et al. J. Am. Ceram. Soc. 1997 80(12):2987-96]. This oxide fiber, when used in an oxide matrix, circumvents the problem of high temperature oxidation [Kuo et al. J. Am. Ceram. Soc. 1997 80(12):2987-96]. The $LaPO_4$ coating material provides a high-temperature oxide-constituent composite with an inherently weak interface [Morgan, P.E.D. 1996 U.S. Patent 5,514,474]. However, problems with coating of oxide fibers

with monazite exist. A higher specific weight of oxide composites in comparison with silicon carbide CMCs is also disadvantageous for aerospace applications. Any oxide coating on a nonoxide fiber and/or in a nonoxide matrix creates a thermodynamically unstable system that will degrade in the process of high-temperature manufacturing of the composite.

Accordingly, there is a need for improved ceramic matrix composites less vulnerable to oxidation and consequent embrittlement when mechanical and thermodynamic loads become large enough to crack the matrices.

10 Summary of the Invention

An object of the present invention is to provide an interface composition or coating for ceramic fibers of ceramic matrix composites, said interface composition or coating comprising boron-aluminum-nitride.

Another object of the present invention is to provide a ceramic matrix composite comprising ceramic fibers coated with boron-aluminum nitride.

Another object of the present invention it to provide methods for production of a ceramic matrix composite comprising ceramic fibers coated with boron-aluminum-nitride.

Brief Description of the Figures

Figure 1(a), 1(b) and 1(c) show the oxidation of carbon, boron nitride and boron-aluminum nitride (BAN) interphases, respectively.

Figure 2 shows the thermodynamical calculation in a BN-AIN system of the present invention.

Figure 3 shows a phase diagram of an $\text{Al}_2\text{O}_3\text{-B}_2\text{O}_3$ system of the present invention.

Detailed Description of the Invention

The most vulnerable component of the ceramic matrix composites is the interphase that separates the fiber and the matrix. It is most desirable for the interphase to be an oxidation-resistant material. However, available interphases for CMC systems such as the SiC/CMC have proven ineffective at high temperatures. There is no fiber coating currently available that can provide protection to the fiber and maintain its debond characteristics for the desired lives (1000 hours).

The present invention provides a new interface composition comprising boron-aluminum-nitride (BAN) and methods for production of the interface composition via coating ceramic fibers with a boron-aluminum-nitride (BAN) nanocomposite coating. The BAN coating of the present invention provides oxidation protection for long-fiber reinforced CMCs because it forms refractory aluminum borates upon oxidation, including $\text{Al}_{18}\text{B}_4\text{O}_{33}$, which is stable till $>1900^\circ\text{C}$ and provides a diffusion barrier, and a boron-containing liquid phase (B_2O_3 at low temperatures or B-Al-O and/or B-Al-Si-O at higher temperatures), which seals cracks in the matrix or along the fiber/matrix interface. The composite with a BAN interface is expected to resist oxidation for 1000 hours over the temperature range from 400 to 1200°C and possibly at higher temperatures. The coating can be obtained using a cost-saving, high temperature chemistry technique easily scaled up for mass production. BAN coatings are compatible with a majority of ceramic fibers and provide fiber debonding and pullout similar to BN. Unlike pure BN, however, BAN is robust and provides oxidation protection in a flow of combustion products. While the oxide coating cannot provide a gettering action to the oxygen, the advantage of this non-oxide coating is that it provides this gettering action while it is oxidizing, thus preventing the oxidation of the underlying fiber. Therefore, from an oxidation standpoint, this non-oxide coating is expected to be better than oxide coatings.

Examples of ceramic fibers of commercial and experimental interest for high temperature aerospace applications which can be coated in accordance with the present invention include, but are not limited to, silicon carbide based fibers such as Nippon Carbon's Hi-NICALON (β -SiC with excess carbon and low oxygen content; Zhang, Z.F. Processing Silicon Carbide Fibers from Organosilicon Precursors, Ph.D. Dissertation. The University of Michigan, Ann Arbor, MI 1994; Strife et al. Cer. Eng. Sci. Proc. 1990 11(7-8):871-919; Okamura et al. Proc. 1st Jap. Int. SAMPE Symp. 1989 929-934; Takeda et al. Ceram. Eng. Sci. Proc. 1993 14(9-10):540-547; Takeda et al. Ceram. Eng. Sci. Proc. 1994 15:133-141; Chollon et al. Structure, Composition and Mechanical Behavior at High Temperature of the Oxygen-Free Hi Nicalon Fiber, High Temperature Ceramic Matrix Composites II, Eds. Evans, A.G., Naslain, R., American Ceramic Society, Westerville, OH, 299-304, 1995] and Ube's TYRANNO fibers [Yajima, S. J. Mater. Sci. 1981 16:1349-55; Yajima, S. Am. Ceram. Soc. Bull. 1983 62(8):893-98], "Hi-Nicalon S" fibers [Takeda et al. Ceram. Eng. Sci. Proc. 1996 4:35-42], powder derived and sintered α -SiC

fiber from Carborundum [Venkateswaran et al. Development of Continuously Sintered Polycrystalline SiC Fiber, Proceedings of 17th Annual Conf. on Composites, Materials and Structures, Cocoa Beach, FL 1993; Pysher et al. High Temperature Properties of Carborundum α -SiC Fibers, HITEMP REVIEW 1992, NASA Conf. Pub. 10104, 1, 22-1-12 1992], Zr-containing TYRANNO fibers [Kumagawa et al. Cer. Eng. Sci. Proc. 1997 18(3):113-118] and a polymer derived and sintered nearly stoichiometric polycrystalline fiber SYLRAMIC from Dow Corning [DiCarlo, J.A., Dutta, S., Continuous Ceramic Fibers for Ceramic Composites. Handbook on Continuous Fiber Reinforced Ceramic Matrix Composites, eds Lehman R., El-Rahaiby S., Wachtman J., Ceramic Information Analysis Center, Purdue University, West Lafayette, Indiana, 1995]. Fibers of these ceramic matrices are expected to be useful in the reinforcement of CMC's in 1000°C to 1400°C temperature range. Other important fibers include the single phase Si-B-(N,C) fibers of Bayer AG [Baldus et al. Trans. Tech. Publ., CMMC 96, Eds Fuentes M., Martinez-Espanaola J.M., Daniel A.M., 177-183, 1996]. Or Textron's SCS-6 and other fibers produced by the chemical vapor deposition on a carbon core.

In a preferred embodiment, the ceramic fibers used in the present invention comprise SiC, as SiC fibers are currently the best choice for composites working at $\geq 1200^\circ\text{C}$. However, boron carbide, boron carbonitride, silicon carbonitride and other carbide-containing fibers can be used. Chopped fibers, short fibers (whiskers) or nanofibers (nanotubes) can be coated in a similar way to continuous fibers or fabrics.

BAN material for coating of the ceramic fibers can be obtained as a heterophase composition comprising either a mixture of boron nitride and aluminum nitride or boron nitride and solid solution of BN-AlN structure of AlN. Plate-like crystals of boron nitride in such compositions ensure a low friction coefficient and easy sliding. High thermal conductivity and low thermal expansion result in a high thermal shock resistance of BN-AlN ceramics. For example, when BN-Si₃N₄ composites survived 40 cycles 20-2500°C, BN-glass up to 78, than BN-AlN survived 98 [Dubovik, T.V., Methods of Formation, Properties and Application of Nitrides, Kiev, ONTI, IPMS, Academy of Science of USSR, 381, 197]. Therefore, it is expected that BAN composition will provide debonding of fibers, improve thermal shock resistance of composites and serve properly as a weak interphase between a ceramic fiber such as SiC_f and the matrix.

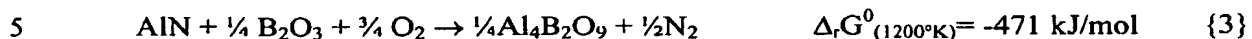
Oxidation of boron and aluminum containing ceramics leads to formation of aluminum borates via alumina and boria. The aluminum borates provide a self-healing coating which arrests cracks and prevents oxidation of the fibers in the range from 450 to >1950°C so that there is no degradation of the fiber strength and no recession of the fiber-matrix interphase (see Figure 1). In the case of alumina forming materials, interaction of alumina with B_2O_3 results in the formation of stable refractory aluminum borates $2Al_2O_3 \cdot B_2O_3$ and $3Al_2O_3 \cdot 4B_2O_3$ and prevents the loss of B_2O_3 due to its vaporization [Schneider et al. Key Engineering Materials 1996 113:49-58; Gogotsi et al. J. Mater. Sci. Lett. 1992 11:308-311]. Further, it has been shown that liquid B_2O_3 can seal cracks in the oxide scale and improve oxidation resistance of boron-containing ceramics at very high temperatures [Gogotsi et al. J. Mater. Sci. Lett. 1992 11:308-311]. In addition, coatings containing AlN and boron compounds form self-healing oxide scales [Courtois et al. J. Phys. III 1993 3(C2):843-853; Gogotsi et al. Key Engineering Materials 1997 132-136:1600-1603] thus indicating their usefulness for oxidation protection of C/C and C/SiC composites.

Accordingly, the use of BAN as an interphase in a CMC such as a SiCf/CMC can prevent high temperature oxidation of the interphase while retaining good debonding properties of BN. The thermodynamical calculation depicted in Figure 2 shows direct evidence that AlN will decompose in the first turn, thereby preventing BN from further oxidation, and create self-healing protective compounds of aluminum borates.

The oxidation protection mechanism of the BAN interface of the present invention is based primarily on the crack sealing concept. The protection mechanism can be understood from the analysis of the phase diagram of Al_2O_3 - B_2O_3 system (see Figure 3) and chemical reactions of BN and AlN with oxygen. Upon heating in air or combustion products, boron oxide is formed. Since its oxidation starts above 450°C, it first forms a liquid phase.

From purely thermodynamic considerations, liquid boron oxide can react either with AlN or with Al_2O_3 . However, the formation of the two borates is favored in case of the reaction between boron oxide and alumina.

The free energy of formation of $\text{Al}_4\text{B}_2\text{O}_9$ (Eq.2) is 12 kJ/mol in comparison with 471 kJ/mol in the case of oxygen presence (Eq.3).



The free energy change in formation of $\text{Al}_{18}\text{B}_4\text{O}_{33}$ from oxides (Eq. 4 and 5) is -10 kJ/mol in comparison with the -469 kJ/mol for the interaction with AlN (Eq. 5).



The free energy changes of reactions {2} and {4} on one hand, and reactions {3} and {5} on the other hand are very similar. Consequently, the formation of both borates can occur with the same thermodynamic probability, depending on the local $\text{Al}_2\text{O}_3/\text{B}_2\text{O}_3$ ratio. As soon as B_2O_3 is formed, it reacts with AlN by reaction {3}, thus yielding $\text{Al}_4\text{B}_2\text{O}_9$ that
 15 forms a solid diffusion barrier at the BAN/liquid boria interface and provides a protective mechanism in the temperature range of 450 to 1000°C. Accordingly, a typical protecting layer consisting of a solid phase (reaction, diffusion and erosion barrier) and a liquid phase (crack/pores sealant) forms from the very beginning of the oxidation. Thus, the composite is protected even at relatively low temperatures when low temperature degradation of
 20 composites with BN or carbon interphases unrelated to oxidation, also referred to as pesting, can occur [Luthra, K.L. J. Am. Ceram. Soc. 1997 80(12):3253-57].

$\text{Al}_4\text{B}_2\text{O}_9$ melts above 1000°C (Figure 3) releasing some boria and providing a second protective mechanism at temperatures exceeding 1000°C. Thus, if the composite is heated to temperatures above 1000-1050°C, the solid protective layer of $\text{Al}_4\text{B}_2\text{O}_9$ will
 25 become thinner, but it will not disappear. A very stable (melting point >1950°C) $\text{Al}_{18}\text{B}_4\text{O}_{33}$ will be formed and will protect the BAN interphase at temperatures exceeding the working temperature of the fiber and of most matrices. For example, if the oxidation temperature is > 1150°C, or water vapor is present or erosion by the flow of combustion products occurs, pure BN interface disappears at a very high rate, unless protected by the
 30 oxidation products of the matrix. In the BAN interface of the present invention, however, this will not happen even if an oxide matrix is used because a low activity of boria in $\text{Al}_{18}\text{B}_4\text{O}_{33}$ will keep B_2O_3 bonded and will prevent the degradation of the composite. In

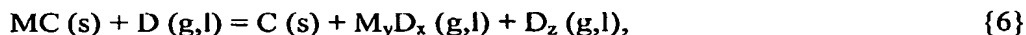
case of an oxidizable matrix (e.g. SiC or Si₃N₄), a protective aluminoborosilicate phase will be formed that can supply additional protection due to the presence of a crack-sealing viscous silicate phase at temperatures above 1200°C. Crystallization of mullite is possible from this phase at higher temperatures. Since aluminoborosilicate (Nextel 312) fibers
5 work well in composites, also at high temperatures, it is believed that oxide layers with a similar composition will be compatible with most of composite matrices and stable up to very high temperatures.

Thus, it is believed that a BAN coating on a ceramic fiber, particularly SiC fibers, will provide an interface with appropriate mechanical properties and the oxidation
10 resistance for utility in ceramic matrix composites. Composites comprising the BAN interface are expected to be useful in high temperature applications in oxidizing environments such as aerospace applications.

In a preferred embodiment, the BAN coating comprises AlN nanodispersed in BN. This nanodispersion improves oxidation resistance (comparable oxidation rate of AlN and
15 BN and uniform propagation of the reaction front) and optimizes mechanical properties of the interface composition. This coating can also contain carbon or oxygen. Aluminum oxide or oxynitride can be formed instead of AlN because they will produce the same protective borate layer upon oxidation.

Various methods are available for applying the BAN coating of the present
20 invention. In one embodiment, a method for synthesis of carbon coating on silicon carbide fibers by extraction of metal from carbide by either supercritical water or halogens and their compounds is used. This extraction method has been described in detail by Gogotsi et al. [Key Engineering Materials 1997 132-136:1600-1603; Formation of Carbon Coating on Carbide Fibers and Particles by Disproportionation Reactions, NATO ARW
25 "Advanced Multilayered and Fiber-Reinforced Composites", *Kluwer Academic Publishers*, 217-230, 1998; J. Mater. Chem. 1997 7(9):1841-1848; Nature 1994 367:628-630; Hydrothermal Synthesis of Carbon Films on SiC Fibers and Particles, in H. Hausner, G.L. Messing and S.-I. Hirano (eds.), *Ceramic Processing Science and Technology*, Ceramic Transactions, Vol. 51, Am. Ceram. Soc., Westerville, OH, 243-247,
30 1995]. The most important feature of this method is that the carbon layer is not deposited on the surface, but rather the surface of SiC is transformed into carbon. Therefore, an extremely uniform coating with good adhesion is formed.

A schematical etching reaction leading to the formation of carbon on the surface of carbides can be written as follows:

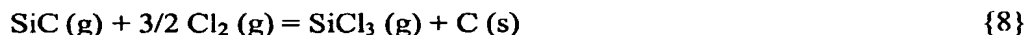


where MC is a metal carbide, D is a gaseous or liquid etchant, M_yD_x is a gaseous or soluble etchant fragment species, and D_z is other possible etchant fragment species. Thermodynamic analysis shows that a number of compounds can act as etchants. In particular, supercritical water [Gogotsi et al. Formation of Carbon Coating on Carbide Fibers and Particles by Disproportionation Reactions, NATO ARW "Advanced Multilayered and Fiber-Reinforced Composites", *Kluwer Academic Publishers*, 217-230, 1998] and halogens [Gogotsi et al. Key Engineering Materials 1997 132-136:1600-1603] have been predicted to extract metals from carbides under selected temperature, pressure and concentration conditions. Extraction of metals from carbides by halogens (F_2 , Cl_2 , Br_2 and I_2) or their compounds (HF , CCl_4 , $CHCl_3$, etc.) can lead to the formation of free carbon. This method is more versatile than hydrothermal synthesis and it requires a relatively simple experimental setup.

Thermodynamic analysis of the reaction products in the system SiC/chlorine containing gases has been conducted in the temperature range 300-1300°C using a Gibbs energy minimization program. Thermodynamic simulation [Gogotsi et al. Formation of Carbon Coating on Carbide Fibers and Particles by Disproportionation Reactions, NATO ARW "Advanced Multilayered and Fiber-Reinforced Composites", *Kluwer Academic Publishers*, 217-230, 1998] demonstrated that carbon formation is expected with Cl_2 and other halogens. In the system of SiC/ Cl_2 , the reaction



is most favorable thermodynamically, and at higher temperatures (above 900°C) the thermodynamic probability of the reaction



increases. Additionally, if oxygen impurities are present, $SiO(g)$, $CO(g)$, $CO_2(g)$ and $SiO_2(s)$ can be formed.

As a result of the above reactions, a carbon coating with uniform thickness and a disordered structure can be obtained. This coating is totally adherent to fibers and does not form bridging between individual filaments in the fabric or tows. The thickness of layers depends on process conditions and can vary from several nanometers to several microns.

Since the degree of porosity can be controlled by parameters of the treatment (see Table 1), materials with a specific adsorption capacity can be provided.

Table 1. Specific surface area, S, and size of graphite crystallites, L_a , in SiC treated in Ar/ Cl_2 and Cl_2/H_2 gases

| Experimental conditions | | | Measured specific surface of SiC (m^2/g) | Carbon content (%) | Calculated surface area of carbon (m^2/g) | L_a (nm), size of graphite crystallites |
|---|------------------------------|------------|--|--------------------|---|---|
| Gas | Temp. ($^{\circ}\text{C}$) | Time (hrs) | | | | |
| 3.5% Cl_2/Ar | 400 | 7 | 47.8 | 8 | 400 | 2.0 - 2.5 |
| 3.5% Cl_2/Ar | 600 | 8 | 140.0 | 11 | 1163 | 2.4 - 2.6 |
| 3.5% Cl_2/Ar | 1000 | 0 | 989.6 | 98 | 1010 | 2.0 - 4.5 |
| 2% $\text{Cl}_2/2\% \text{H}_2/\text{Ar}$ | 1000 | 72 | 11.5 | < 5 % | 10 | 1.0 - 4.5 |
| As-received SiC powder | | | 13.6 | < 3 % | | 2.0 |

Thin films of carbon can be obtained on SiC fibers or fabrics. Under certain conditions, it is possible to obtain nanoporous carbon layers with very high specific area of about 1000 m^2/g and pore size of 1 nm or less. These films allow for easy impregnation with salts and an uniform nitride coating after nitridation.

Experiments with polymer derived (Tyranno) and CVD(SCS-6) fibers showed that the formation of carbon is very uniform and does not change the shape of fibers. This is indicative of the growth of carbon by extraction of Si from SiC and collapse of the cubic structure of β -SiC to amorphous carbon. Raman spectra similar to that obtained from hydrothermal amorphous carbon have been obtained from the carbon coatings on both types of fibers [Gogotsi et al. Formation of Carbon Coating on Carbide Fibers and Particles by Disproportionation Reactions, NATO ARW "Advanced Multilayered and Fiber-Reinforced Composites", Kluwer Academic Publishers, 217-230, 1998]. This leads to the formation of a BAN nanocomposite material that is expected to have a higher oxidation resistance compared to macro-structured BN/AlN.

Temperatures at about 400-700 $^{\circ}\text{C}$ are required to obtain carbon coating by chlorination. CVD fibers can be coated by chlorination at a lower temperature than is required in the case of hydrothermal treatment. However, since CVD fibers don't degrade

at high-temperatures (up to 1500°C), temperatures as high as 1000-1100°C can be used to produce a carbon coating in a short time. Also, pre-existing carbon coatings on the fibers produced by CVD can be used in BAN synthesis.

- Transformation of carbon to BAN is preferably performed using a commercially
- 5 viable method such as that proposed for producing BN thin film on silicon carbide whiskers using inexpensive borate precursors. The method is based on the reaction between boron and aluminum salts with carbon and ammonia upon heating. Three different BN precursors, sodium borate decahydrate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), ammonium borate tetrahydrate ($(\text{NH}_4)_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$), and boric oxide (B_2O_3) have been applied.
- 10 $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ can be used to obtain AlN thin films on silicon carbide fibers [Brown, S.E., Partch, R.E. Abstracts of the 28th Annual Meeting of the Fine Particle Society, Dallas, Texas 1998]. However, in that method, samples were contaminated with sodium, which decreases the high-temperature strength and oxidation resistance of the fibers, and no uniform coatings could be produced.
- 15 Thermodynamic analysis showed that B_2O_3 consumption starts at about 800°C and all boron oxide would be transformed to BN below 1200°C. Very similar results have been predicted for the formation of AlN. Due to a very fine (nanoporous) carbon coating, serious kinetic limitations of the reaction are not expected so that synthesis can be conducted at 1100-1200°C.
- 20 During the reactions, carbon layer absorbs the precursor melt, which further undergoes nitridation with ammonia at elevated temperatures. Carbon promotes the conversion of B_2O_3 and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ to BAN and forms carbon monoxide as a byproduct. As the reaction progresses and BAN is formed, the porous carbon layer is completely or partly consumed resulting in a carbon-free or carbon-containing coating.
- 25 This can be controlled by changing the process parameters. Control of the ceramic coating thickness depends on the quantity and the physical characteristics of the carbon layer obtained by selective etching in halogens. Nitridation was examined over a range of temperatures for varying amounts of time. Specifically, temperatures of 1100, 1200 and 1300°C for 10, 30, 60, 150 and 480 minutes each were examined. In each case BN was
- 30 formed on the surface of all samples. The 10 minute reaction, in comparison to the 60 minute reaction, had less crystalline h-BN and a smaller crystalline size, suggesting that longer reaction times and nitridation temperatures may increase the quantity of crystalline h-BN.

A similar chemical approach has been used by Allied Signal company to obtain BN coating on boron-containing alumina-silica (Nextel 312) fibers, which were thermally treated in the ammonia atmosphere [Campbell, S.S. and Gonszy, S.T. Ceram. Eng. Sci. Proc. 1994 327-336; Campbell, S.S. and Gonszy, S.T. Ceram. Eng. Sci. Proc. 1994 337-343]. During this treatment, boria diffuses to the fiber surface and can be reacted with ammonia to form a thin BN coating on the surface. However, the required reaction temperature is higher than that of the $B_2O_3 + C + NH_3$ interaction and this process is not applicable to SiC fibers.

Thermodynamic calculation shows that synthesis of AlN from aluminum salts and ammonia is feasible and that the suitable temperature for the reaction is approximately 700-900°C. Further, BN stays in equilibrium with AlN during the synthesis of AlN to produce a BN-AlN mixture on the carbon coated SiC first. AlN is produced after BN.

A suitable content of AlN (or AlON) in BN for the C-SiC coating is in the range of about 40-400% . At lower temperature (<1000°C), the product of such coating in the oxidized atmosphere is mainly $Al_4B_2O_9$, while the oxidized product becomes $Al_{18}B_4O_{33}$ in relatively higher temperature (>1000°C). Both of these oxidation products are desirable for fiber-reinforced CMCs to form a solid diffusion barrier and protection layer at the interface of the reinforced fibers and matrix. Meanwhile, B_2O_3 (glass) may also form in the liquid phase from the very beginning of the oxidation and acts as a crack/pores sealant to provide additional oxidation-resistance to the reinforced ceramic fibers in this matrix.

The following nonlimiting examples are provided to further illustrate the present invention.

EXAMPLES

Example 1: Materials

Materials used include SiC fibers such as NICALON (Nippon Carbon, Japan), TYRANNO (Ube Industries, Japan), or SYLRAMIC fibers. Experiments are conducted on single fibers and fiber tows and fabrics. Examples provided here use Tyranny ZMI fiber,

Example 2: Synthesis of Coatings

Ceramic fibers are coated with BAN coatings comprising 0% BN-Al(O)N to
5 100%Al(O)N0-BN.

(1) Chlorination


The process for synthesis of intermediate carbon films on SiC utilizes a chlorine
extraction method. The carbon coatings obtained are conformal and do not change the
10 shape or surface quality of the samples. They have nanoscale porosity, and excellent
adherence to SiC.

Tyranno ZMI SiC fibers produced by Ube Industries, Japan, (~10 μ m in diameter)
were treated in pure Cl₂ with gas flow of 10sccm for 3 hours at 550°C and 650°C in
atmospheric pressure to form carbon coatings on fibers with the thickness of ~ 0.15 μ m and
15 ~1.5 μ m, respectively.

(2) Infiltration

Boric acid was used as the most economical precursor for the synthesis of BN.
Moreover, unlike other precursors, it does not contaminate the samples by introducing
20 metal impurities. A vacuum chamber was used to infiltrate saturated H₃BO₃ solution into
the carbon layer formed on the SiC. The reduced pressure in the chamber induced the
release of the gases absorbed on the surface of the nanoporous carbon layers, so that better
infiltration could be achieved.

The CDC coated fibers were placed in the vacuum infiltration chamber and
25 pumped down for about 30 minutes. They were then infiltrated with saturated H₃BO₃
solution at 100°C. Cold distilled water was used to wash out the excess crystallized



H₃BO₃ from the fiber surface at room temperature. To achieve good infiltration effect for the nanoporous carbon coating, this step was repeated two or three times.

(3) Nitridation

5 Infiltrated CDC-coated SiC fibers were loaded in a quartz holder and put into a horizontal quartz tube furnace. Before each experimental run, the furnace was purged with argon for at least 30 minutes. Then the furnace was heated to the desired operating temperature at a rate of 10°C/min with ammonia (grade 4: purity 99.99%, BOC gases) flowing into the reaction tube at a flow rate of 10sccm. The sample was held at the set
10 temperature for a period of time to secure the completion of the reaction, and then cooled down in the furnace under the ammonia flow for protection. The specific treatment temperatures and times for different SiC samples are shown in Table 1.

Example 3: Studies of Coating Thickness

15

The coating thickness is examined by Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM).

Example 4: Studies of Coating Composition


20

The coating Composition was studied by using Energy Dispersive Spectroscopy (EDS) in SEM..

Example 5: Determination of Fiber Strength

25

Fiber strength is determined by tensile testing of single fibers at room temperature. Changes in Young's modulus and strength after coating as well as interfacial sliding are used as parameters of strength after coating. The coated fibers were compared with untreated fibers by conducting tensile tests for single fibers according to ASTM 3375-79.



10 to 20 fibers were tested for each sample sample. Room temperature tests were performed with a gauge length of 25 mm using paper frame holders. The average value of the diameter of each kind of fiber was determined by SEM images.

5 Example 6: Oxidation Testing

Oxidation tests are performed on single fibers followed by analysis of cross-section changes and tensile strength measurement.

What is Claimed is:

1. An interface composition or coating for ceramic fibers of ceramic matrix composites, said interface composition or coating comprising boron-aluminum-nitride.

5 2. The interface composition or coating of claim 1 wherein aluminum nitride (AlN) or aluminum oxynitride (AlON) is nanodispersed in boron nitride.

3. A ceramic matrix composite comprising ceramic fibers coated with boron-aluminum nitride.

10

4. The ceramic matrix composite of claim 3 wherein the ceramic fibers are coated with aluminum nitride nanodispersed in boron nitride.

15 5. A method for coating a ceramic carbide fiber with boron-aluminum-nitride comprising

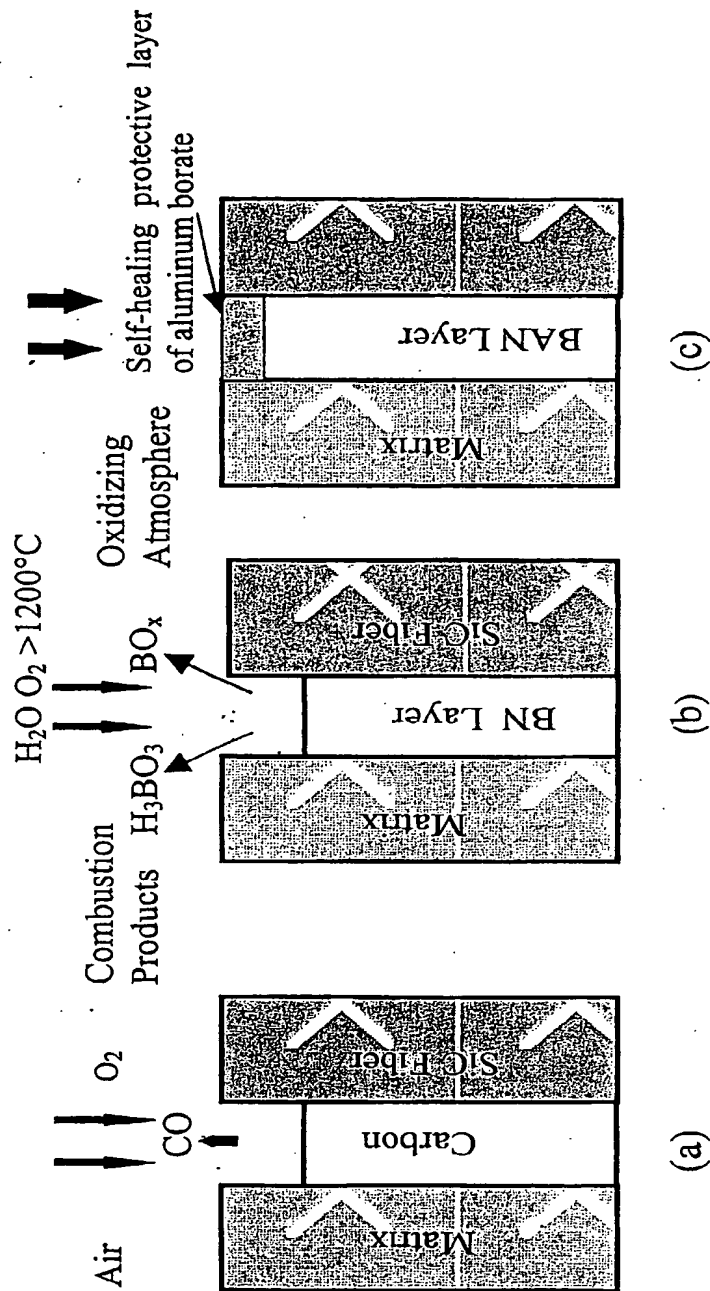
(a) extracting metal from the ceramic carbide fiber to form a thin uniform carbon layer on the ceramic carbide fiber; and

20 (b) transforming the carbon layer on the ceramic carbide fiber to boron-aluminum-nitride by reacting the carbon layer with boron and aluminum salts in the presence of ammonia and heat so that the carbon layer is consumed and the carbide fiber is coated with boron-aluminum-nitride.

DRE-0075**20****PATENT****ABSTRACT**

Boron-aluminum-nitride interface compositions and coatings for ceramic fibers used in ceramic matrix composites are provided. Also provided are methods for production of boron-aluminum-nitride coated ceramic fibers.



**Figure 1**

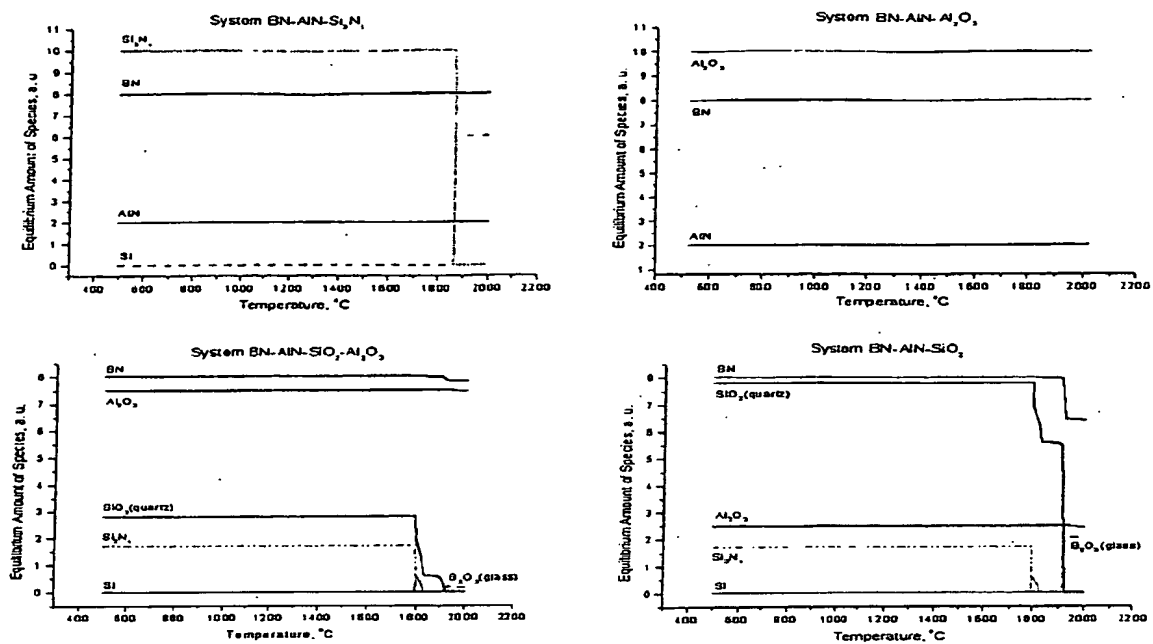
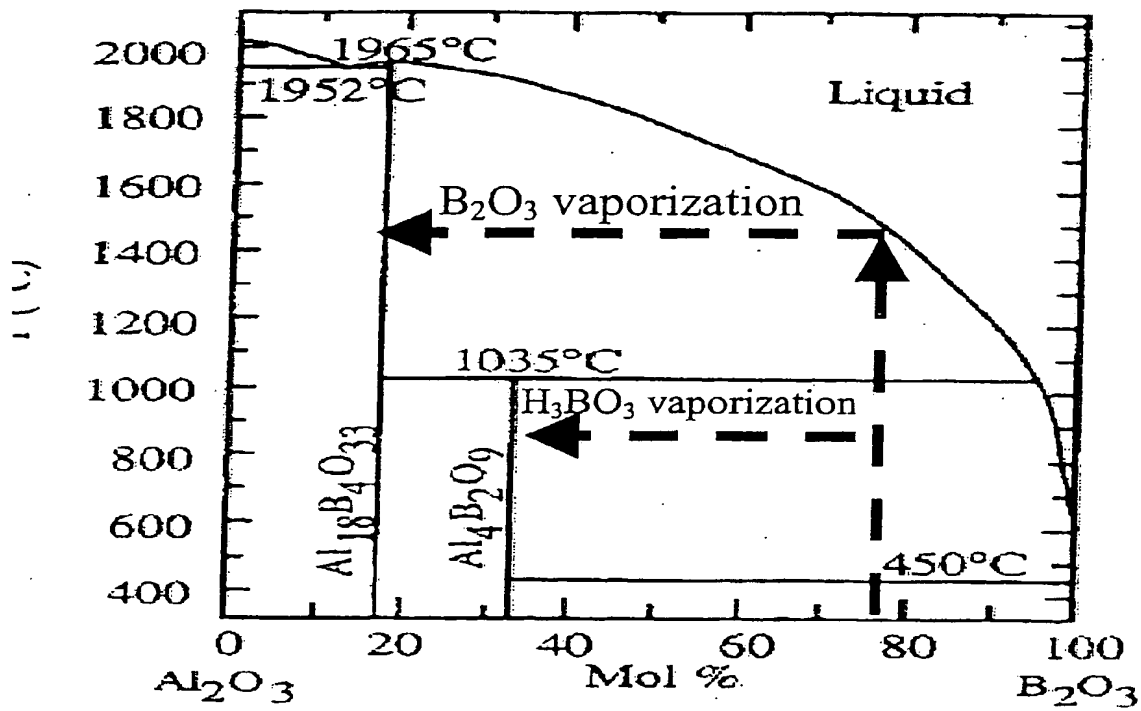


Figure 2

**Figure 3**

Document made available under the Patent Cooperation Treaty (PCT)

International application number: PCT/US04/012965

International filing date: 28 April 2004 (28.04.2004)

Document type: Certified copy of priority document

Document details: Country/Office: US
Number: 60/466,556
Filing date: 28 April 2003 (28.04.2003)

Date of receipt at the International Bureau: 11 April 2005 (11.04.2005)

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b)



World Intellectual Property Organization (WIPO) - Geneva, Switzerland
Organisation Mondiale de la Propriété Intellectuelle (OMPI) - Genève, Suisse